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FeO and H_2O and the homogeneous accretion of the earth

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ABSTRACT

We present new shock devolatilization recovery data for brucite ($Mg(OH)_2$) shocked to 13 and 23 GPa. These data combined with previous data for serpentine ($Mg_3Si_2O_5(OH)_4$) are used to constrain the minimum size terrestrial planet for which planetesimal infall will result in an impact-generated water atmosphere. Assuming a chondritic abundance of minerals including 3-6%, by mass water, in hydrous phyllosilicates, we carried out model calculations simulating the interaction of metallic iron with impact-released free water on the surface of the accreting Earth. We assume that the reaction of water with iron in the presence of enstatite is the prime source of the terrestrial FeO component of silicates and oxides. Lower and upper bounds on the terrestrial FeO budget are based on mantle FeO content and possible incorporation of FeO in the outer core. We demonstrate that the iron-water reaction would result in the absence of atmospheric/hydrospheric water, if homogeneous accretion is assumed. In order to obtain $\sim 10^{25}$g of atmospheric water by the end of accretion, slightly heterogeneous accretion with initially 36% by mass iron planetesimals, as compared to a homogeneous value of 34% is required. Such models yield final FeO budgets, which either require a higher FeO content of the mantle (17 wt. %) or oxygen as a light element in the outer core of the Earth.

INTRODUCTION

A key feature of homogeneous planetesimal accretion models of the terrestrial planets is the interaction of metallic iron with free water on the surface of the growing planets [1]. Previously, we have shown [2,3] that structural water, if contained in chondrite-like planetesimals could provide the major source of free water on the accreting metallic iron-free terrestrial planets. In these models we considered impact of metal free planetesimals onto the growing planet. Shock heating leads to the release of structural volatiles, which will be added to a growing proto-atmosphere. In previous models we attempted to describe the following processes:

(i) the shock-induced dehydration of water-bearing minerals contained in planetesimals via impact onto a growing planet;

(ii) reincorporation of shock-released atmospheric water into the planet as a result of reactions of water with anhydrous surface minerals (mainly forsterite and enstatite), and formation of hydrous phyllosilicates;

(iii) the shock-induced release of structural water from previously formed hydrous minerals (via process (ii)) due to the subsequent impact of infalling planetesimals.

We examined the effect of varying parameters in a model which would allow the formation of a primary atmosphere/hydrosphere during the accretion of the Earth (e.g. Fig. 1). For example, assuming homogeneous accretion at a uniform rate of chondritic composition planetesimals in a time, τ, yields free water only after ~ 0.8 τ (Table 1). Initially, all the water is used up in hydrating anhydrous silicates and only during the latter stages of accretion are impact velocities sufficiently high to release water from phyllosilicates in shocked planetesimal and regolith material to produce a predominantly water atmosphere of impact origin. These processes then lead to depletion of water in the interior volume of the earth and concentration of water within the uppermost part of the accreting planet. Continuing impacts by infalling planetesimals produce (depending on the dehydration efficiency) abundant free water at later times. The point at which an atmosphere starts to form is thus controlled by a parameter which we called "dehydration efficiency". This is defined as the percentage of the water which could be released by a given impact actually escapes the accreting regolith to be added to the proto-hydrosphere/atmosphere [3].

Previous model calculations were based on theoretically derived, critical shock pressures for the release of structural water in brucite ($Mg(OH)_2$) and serpentine ($Mg_3Si_2O_5(OH)_4$) [2,3]. These two minerals are thought to be representative of the major sources of water in carbonaceous chondrites [3,4] and thus in chondrite-like planetesimals. However, we did not model the interaction of shock-released, atmospheric water with the free iron delivered in planetesimals.

The aim of the present paper is thus twofold. We firstly will present data which quantitatively define shock-induced water loss as a function of shock pressure for brucite and compare these to recent results for serpentine(s). Secondly, we will describe model calculations which simulate iron-water interaction in the course of the Earth's accretion.

SHOCK-INDUCED DEHYDRATION OF BRUCITE AND SERPENTINE

We performed shock recovery experiments on brucite (Table 2) and serpentine [5] and determined the amount of post-shock water of the shocked samples by use of a thermogravimetric analyser (for experimental details, see [5]). Comparison with initially present structural water yields the amount of shock induced-water loss as a function of shock pressure (Figure 2). Although the data shown in Figure 2 approximately agree with previous calculations predicting the pressure required for the complete loss of structural water from these minerals [2,3], they now allow more precise definition of the onset of shock-induced dehydration. Shock pressures in both brucite and serpentine can be related to impact velocities needed to reach these pressures. Assuming that infall impact velocities equal the increasing escape velocities of a growing planet, we can relate relative size, r/R, and relative mass m/M (R,M = final radius and mass of a planet; r,m = radius and mass of the growing planet) to shock pressures in both brucite and serpentine. Thus, we can replace the pressure axis in Figure 2 with a r/R - or a m/M - axis (Figure 3). As can be seen, complete water loss in serpentine minerals occurs when Venus and Earth have grown to ~half their radius and ~10% of their final mass. On Mars, impact velocities are never high enough to induce complete impact-induced dehydration of serpentine during its accretion.

IRON-WATER INTERACTION DURING ACCRETION

a) Boundary conditions for model calculations

Our model calculations are based on accretion models of Weidenschilling [6,7]. He describes the mass increase of the growing Earth as a function of time and derives a total accretion time of $\tau = 1.6\times10^{8}$ yrs.

We assume a chondritic composition of the planetesimals and specifically use 8% anorthite, 23% enstatite, 35% forsterite and 34% metallic (nickel-) iron in our calculation. We assume that 3 wt. % of the accreting material is structural water bound in water-bearing phyllosilicates in the silicate fraction of the planetesimals [3]. This composition is derived from a mixture of 15% low- and 85% high-temperature condensates [1] and is held constant for calculations simulating homogeneous accretion of the Earth.

Chemical analyses of minor mantle-derived ultramafic nodules demonstrate that minor siderophile element abundances (e.g. Ni, Ir, Os, Au) occur in near chondritic proportions [8,9,10,11]. Moreover, no physical model of core formation allows chemical equilibrium of core and mantle material, either at the surface, or at depth [12,20,21]. As a consequence, chemical equilibrium between core and mantle could not have been maintained during the entire accretion process. This in turn requires either incomplete reactions between homogeneous components or a slightly heterogeneous accretion [14]. The latter implies iron and other high temperature condensates will be enriched during the earlier parts of the accretional sequence. We assume the initial metallic iron fraction in initial planetesimals varies from the homogeneous value of 34% to an extremely heterogeneous model of 95% iron.

As an extreme, we assume that the entire FeO (represented in the upper mantle as fayalite and ferrosilite) budget of the Earth is derived due to reactions of metallic iron with water. Thus no iron is assumed to be accreted as Fe^{2+} or Fe^{3+} in oxides or silicates. The principal reaction between iron, enstatite, and water is:

$$MgSiO_3 + Fe + H_2O \rightarrow \frac{1}{2}Mg_2SiO_4 + \frac{1}{2}Fe_2SiO_4 + H_2\uparrow \tag{1}$$

enstatite + iron + water → forsterite + fayalite + hydrogen

This reaction is assumed to occur in the regolith of the accreting planet. Thus, water is lost in this process and hydrogen escapes via Jean's loss [15]. As can be seen, for a chondritic composition of planetesimals in a homogeneous model, there will always be more metallic iron than needed to react with the available water. Hence, by the end of accretion, no free water will be left in such a model.

Recently, Fukai and Akimoto [16] and Fukizawa [17] have proposed that the reaction

$$[2/x + 1]\, Fe + H_2O \rightarrow [2/x]\, FeH_x + FeO \qquad (2)$$

takes place at high pressure ($\sim 10^1$ to 10^2 kbar) during the accretion of the earth. Although we have not considered Eq. 2, we infer from our models that <u>all</u> the water which is incorporated during the early stages of accretion (when the mass of the earth was less than 0.2 M) could participate in reaction (2) if the pressure on this material was later increased. This wouid occur as accretion continued and buried this initial water budget. As shown in Fig. 3 the later material would be successively more devolatilized as even higher velocity impacts took place on the growing terrestrial surface.

In order to constrain the preser. terrestrial FeO budget (in the form of the iron component of ferromagnesium silicates) we first consider the FeO bound in the mantle of the Earth. The FeO budget of the (upper) mantle is fairly well constrained by seismological and geochemical data on ultramafic inclusions in mantle derived nodules and compositional models derived from seismic data [18]. A minimum estimate of 8% FeO for the entire mantle yields 3×10^{26}g.

In order to obtain absolute maximum constraint we could also take into account a possible FeO component in the outer core. We know from diamond anvil experiments [19] that above $\sim$10GPa, FeO may produced at high pressures from reactions such as:

$$Fe_2SiO_4(\gamma) \rightarrow 2FeO + SiO_2\ (\text{stishovite}) \qquad (3)$$

The FeO resulting from such disproportionation could by some unspecified process ultimately be incorporated into the core if it became metallic under sufficiently high pressure [1]. In any case, the presence of FeO, resulting from this reaction in the outer core cannot be excluded based on the present data. Based on shock wave studies, Jeanloz and Ahrens [13] conclude that an FeO content of the outer core of up to 45 wt. % is compatible with their data. Taken this amount of FeO, together with the mantle reservoir results in an upper FeO boundary of 1.2×10^{27} g.

b) Modelling techniques

The accretion model of Weidenschilling [6,7] specifie the amount of mass to be added to the growing Earth as a function of time. Depending on the particular model to be computed, i. e. either homogeneous or heterogeneous models with varying initial iron fractions, we determined the amounts of anorthite, enstatite, forsterite, iron, and water to be accreted for each time step in the calculation (Table 3). Iron was added until total amount accreted was equal to the mass of the present core (i.e., for homogeneous models for the entire accretion sequence). As long as iron is being accreted, it reacts with water and the resulting FeO is added to the growing FeO reservoir of the Earth. Once the mass of the accreting iron equals the core mass, we assumed no iron accretion occurs and the accreting water is added to a growing proto atmosphere/hydrosphere. At the same time, FeO production ceases.

In our model calculations, we tried to match either the lower or the upper FeO boundary by simultaneously attempting to form a sizable water reservoir on Earth. This was done by modifying the amount of initially accreting iron (i.e., the degree of inhomogeneity) for a given water content of the accreting silicate planetesimals (Table 3).

c) Model results

Homogeneous accretion models lead to the continuous interaction of water with iron which results in the absence of a sizable terrestrial water budget by the end of accretion (Figure 4). The FeO budget, produced as a result of iron-water reactions lies in-between the lower and upper terrestrial FeO boundary. Hence, we either have to increase the amount of FeO in the mantle to 17 wt. % (as compared to present estimates of 8 wt. %) or FeO becomes a constituent of the outer core [1].

In order to avoid the latter consequence, inhomogeneous accretion with an initial iron fraction of 60% is required (Figure 4). This results in a final FeO value in agreement with the lower FeO boundary but also in a final water reservoir exceeding present estimates for the terrestrial water budget of $\sim 10^{25}$g [3] by almost an order of magnitude.

On the other hand, if we attempt to generate enough FeO to satisfy the upper FeO boundary by means of homogeneous accretion, i.e., with a constant iron fraction of 34%, we have to nearly double the amount of water contained in silicate planetesimals to 6 wt. % (Figure 5). Again, no significant water reservoir would be left by the end of accretion as a result of continuous iron-water interaction (Model 7, Table 3). If we accept a water content of 6% of silicate planetesimals, which would mean, that we increase the amount of low temperature condensates, but want to retain a final FeO budget in agreement with the lower FeO bound, we require inhomogeneous accretion with an iron fraction of 60% among initial accreting planetesimals. This model (#6, Table 3) would result in a final water reservoir exceeding present estimates.

In order to explore the results of an extremely inhomogeneous accretion, models with 95% initial iron planetesimals have been computed for water contents of 3 and 6 wt. % (Figures 4 and 5). Both models result in the rapid growth of the core which leads to a limited interaction of iron with water during a relatively short time span (for the first 0.4 x 10^{6} yrs). Hence, the resulting FeO budget (in both models) lies below the lower FeO boundary (not shown in the figures) and the water reservoir at the end of accretion is well in excess of present estimates.

Our model calculations demonstrated that it seems to be impossible to satisfy either the lower or the upper FeO boundary and simultaneously forming a terrestrial water reservoir in agreement with present estimates. The model which most closely results in a water budget of $\sim 10^{25}$ g is a slight heterogeneous model with 36% of initial iron planetesimals and 3% water in silicate planetesimals (Figure 4). Here, iron accretion prevails during most of the accretional sequence and results in the production of FeO similar to the homogeneous model (see curve "FeO (34%)" in Figure 4). Thus, again, we either have to allow for more FeO in the Earth's mantle, contrary to present estimates, or accept FeO as a constituent of the outer core of the Earth.

CONCLUSIONS

Shock recovery experiments on brucite and serpentine provide quantitative estimates on the amount of shock-induced water loss as a function of impact speed and hence shock pressure. The data agree with earlier estimates for the total release of H_2O and justify conclusions inferred from earlier model studies [2,3]. The present results define more completely the conditions required for an impact generated atmosphere and demonstrate that shock-induced water loss is likely to have occurred on Earth and Venus during most of their accretion, while Mars, mainly due to its smaller mass, should have retained within its interior a greater fraction of its initial volatiles.

Iron-water interactions on the surface of an Earth accreting homogeneously will result in the absence of a water reservoir by the end of accretion and in final FeO content (in ferromagnesian minerals) requiring either higher than usually accepted mantle-FeO content (17 wt %) or the incorporation of FeO into the Earth's core. Our models demonstrate that it is impossible to obtain as little

FeO as 1.2 x 10^{27}g) by homogeneous accretion and also obtaining a terrestrial water budget (~10^{25}g). A slightly inhomogeneous accretion model with an initial iron planetesimal fraction of 36% (as compared to the homogeneous value of 34%) results in the oceanic budget of water by the end of accretion. Such a model is in accordance with proposed accretion scenarios of other researchers [e.g. 10,11,12]. However, the amount of FeO produced in such a model, requires either a higher than usually accepted FeO-mantle reservoir (17% wt % FeO) or oxygen as a light element in the outer core [1].

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Figure Captions

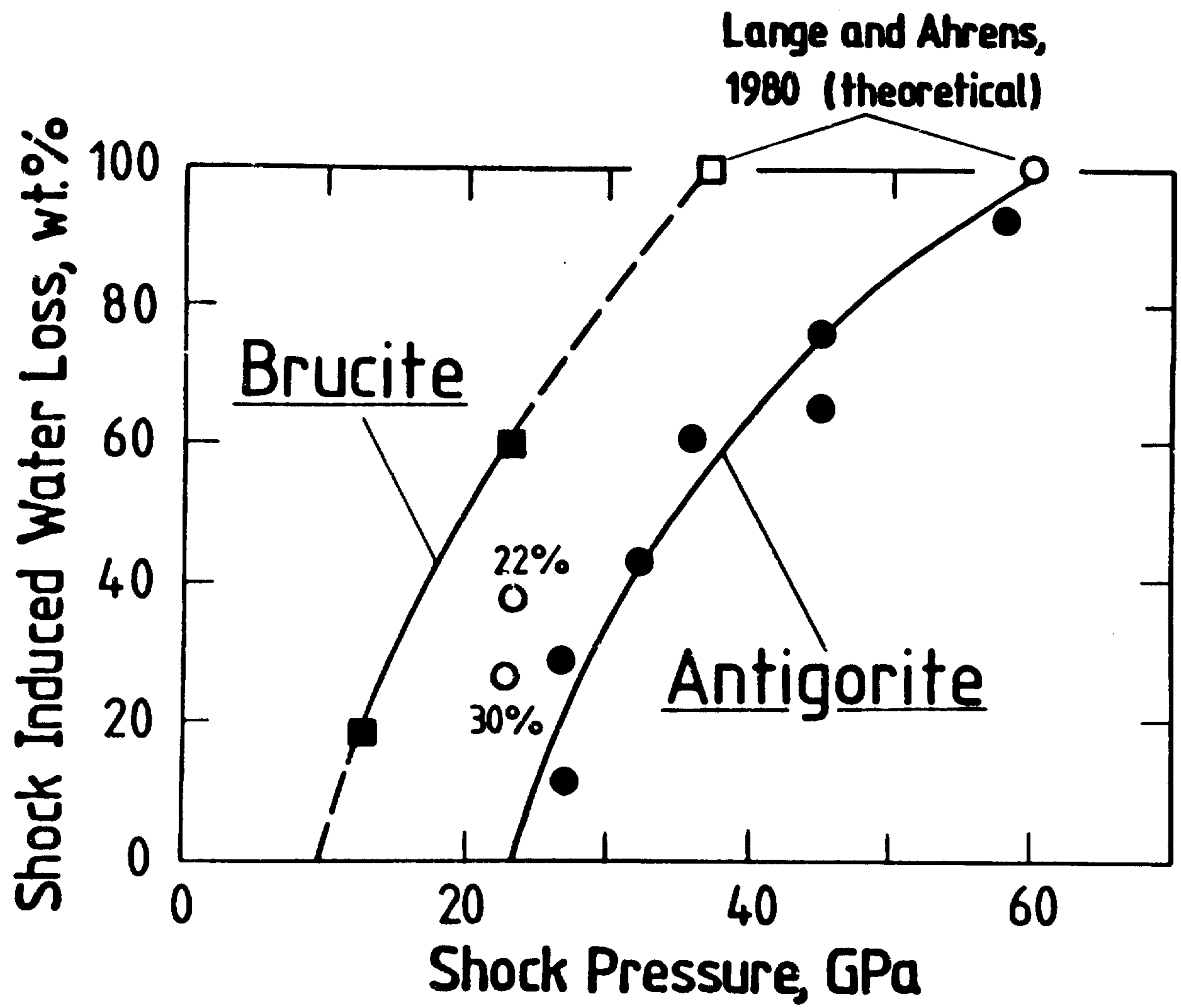
Figure 1. Accumulation of water in a primary atmosphere/hydrosphere as a function of time during accretion for iron-free silicate material and after core formation (τ = total accretion time).

Figure 2. Shock-induced water loss (in wt. % of total amount of initially present water) in brucite and antigorite-serpentine as a function of shock pressure in shock recovery experiments. Theoretical predictions are from [2].

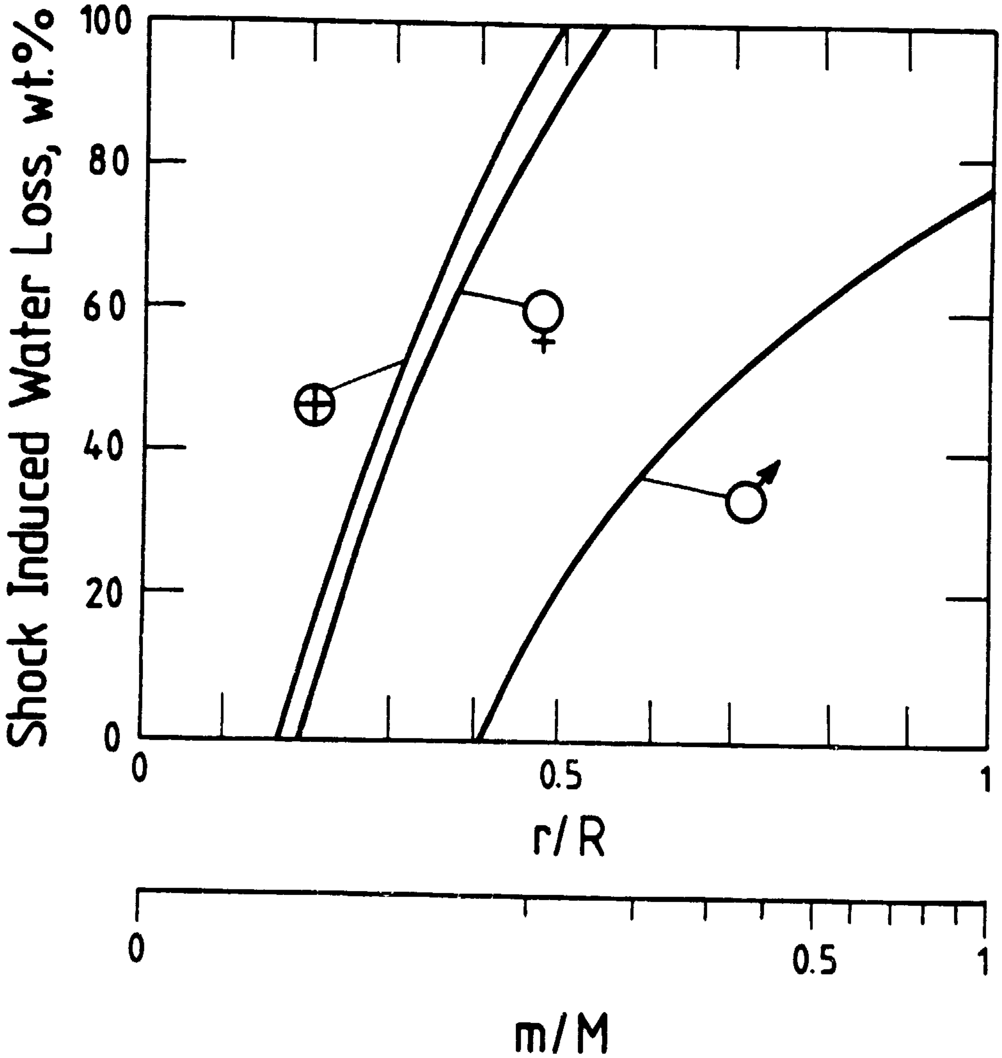
Figure 3. Shock-induced water loss in serpentine as a function of relative size r/R or relative mass m/M of the accreting terrestrial planets. Dehydration takes place when the impact pressures as given in Figure 2 are exceeded. This takes place at different stages in the accretional sequence of Earth (⊕), Venus (♀) and Mars (♂).

Figure 4. Accretion of the Earth (curve "Total Mass") according to a model of [6,7], the growth of a core (curves labeled, Fe), the formation of a terrestrial FeO budget (curves labeled, FeO) and the growth of a terrestrial water reservoir (curves labeled, H_2O) as a function of time (total accretion time, 1.6 x 10^8 yrs). Numbers in parenthesis give the fraction of initially accreting iron. For heterogeneous accretion models (Fe > 34%) iron accretion stops, once the mass of the core is reached (vertical lines) and from this point on, a water reservoir is built up. For these models, formation of FeO (due to interaction of iron with water) also ceases once the core is formed and the FeO content remains constant from this point on (horizonta[illegible]hed line). The water content of infalling planetesimals for all [illegible] these models is 3 wt. %.

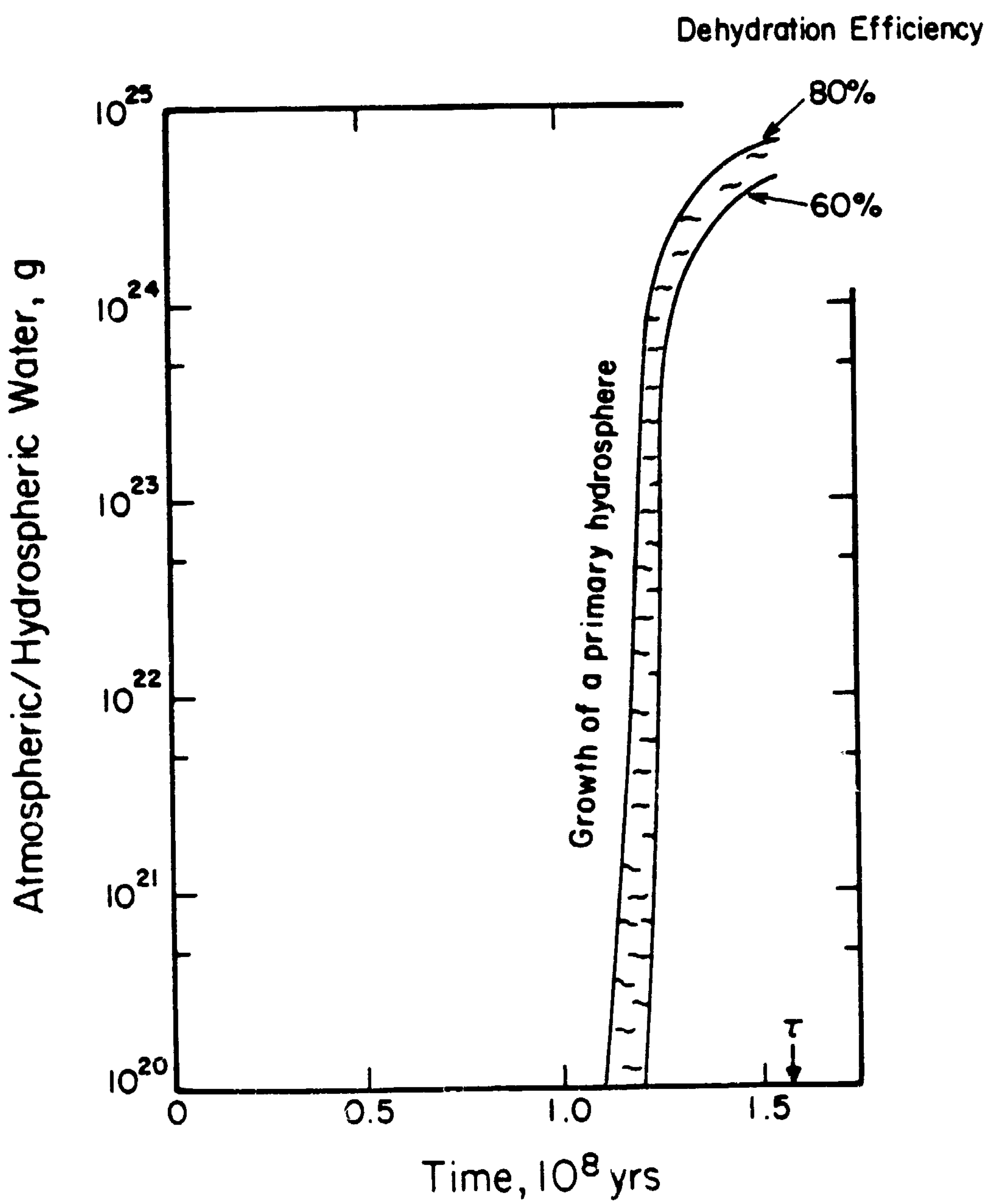
Figure 5. Results of model calculations for which the water content of planetesimals was increased to 6 wt. %. Other details, see Figure 4.



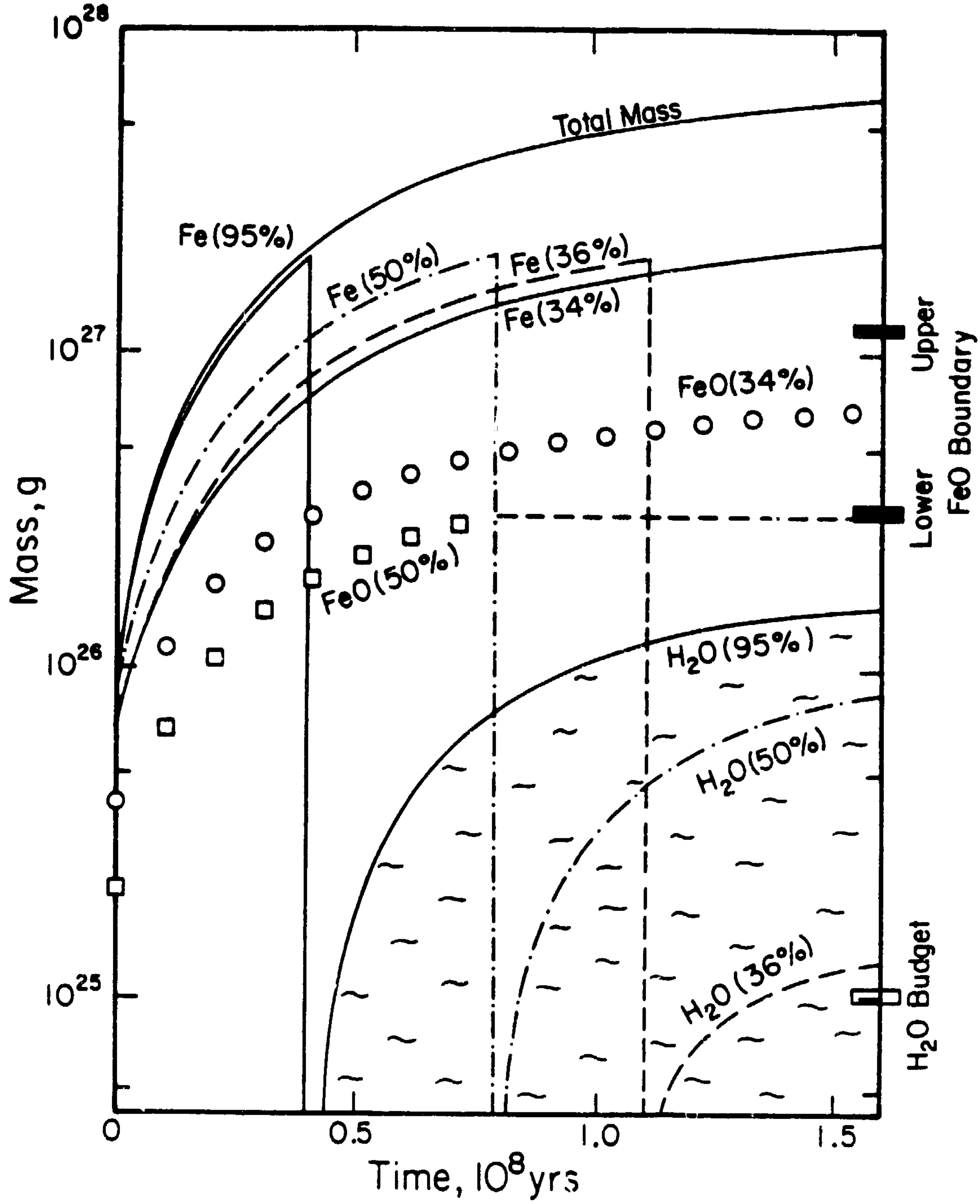
Lange and Ahrens,
1980 (theoretical)
Shock Induced Water Loss, wt.%
100
80
60
40
20
0
Brucite
22%
30%
Antigorite
0
20
40
60
Shock Pressure, GPa



Shock Induced Water Loss, wt.%
100
80
60
40
20
0
0
0.5
1
r/R
⊕
♀
♂
0
0.5
1
m/M



Dehydration Efficiency
80%
60%
Growth of a primary hydrosphere
Atmospheric/Hydrospheric Water, g
10^{25}
10^{24}
10^{23}
10^{22}
10^{21}
10^{20}
τ
0
0.5
1.0
1.5
Time, 10^8 yrs


Total Mass
Fe(95%)
Fe(50%)
Fe(36%)
Fe(34%)
FeO(34%)
FeO(50%)
H_2O(95%)
H_2O(50%)
H_2O(36%)
Upper
Lower
FeO Boundary
H_2O Budget
Mass, g
Time, 10^8 yrs
10^{28}
10^{27}
10^{26}
10^{25}
0
0.5
1.0
1.5

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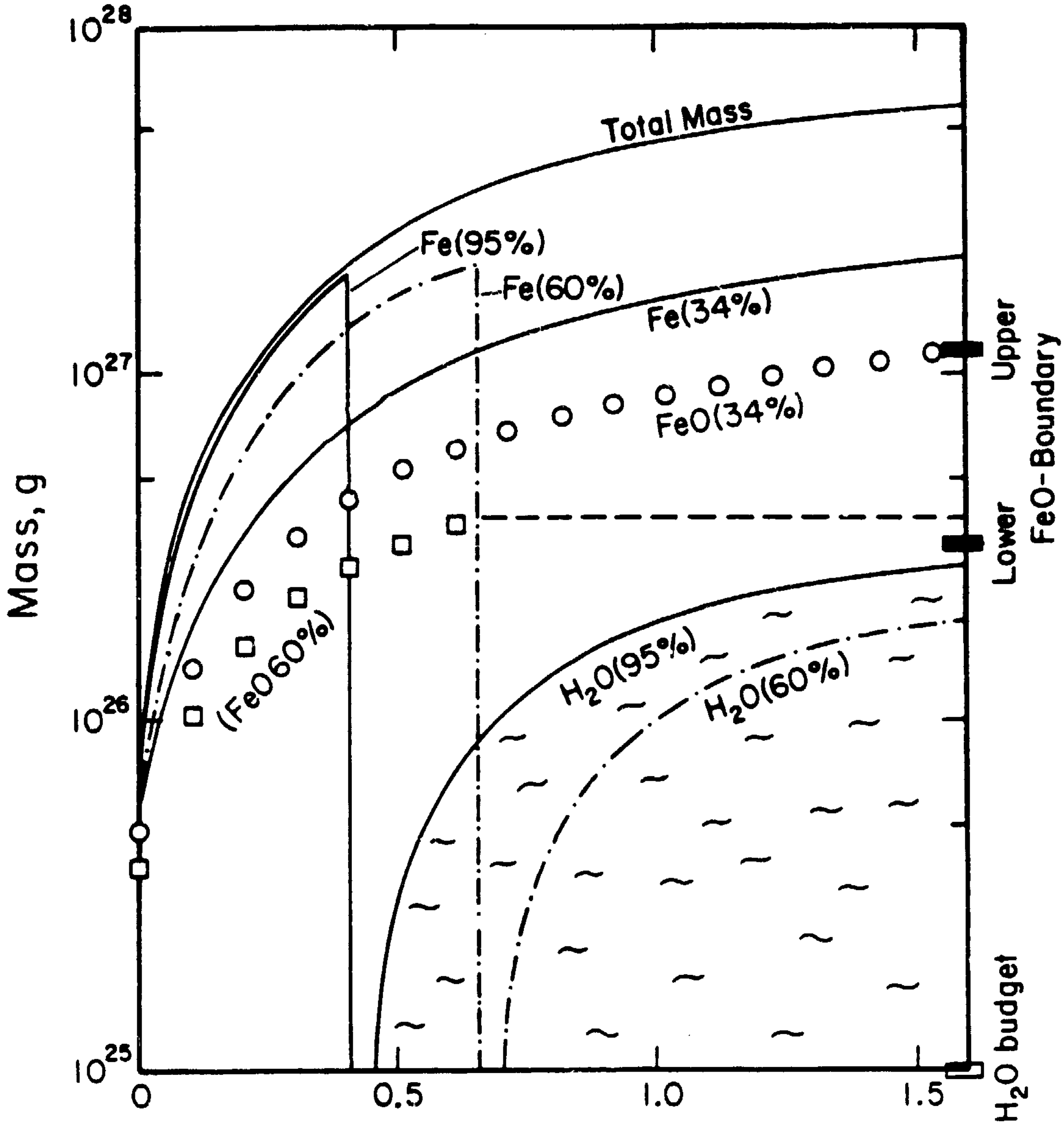

Table 1. Normative composition of Earth-forming planetesimals after [1][1)] and assumed distribution of planetesimal types.

Mineral	Normative amount[2)] wt. %	Planetesimal type	Fraction wt %
Plagioclase	7.6	Anorthite	7.7
Pyroxene	22.3	Enstatite[3)]	22.5
Olivine	35.0	Forsterite[3)]	35.4
Metallic Nickel-Iron	34.1	Iron[4)]	34.4
Apatite	0.12		
Ilmenite	0.34		
Chromite	0.32		
Σ	99.8		100.0

1) Norm calculations based on a composition resulting from a mixture of 15% low- and 85% high temperature condensates as given by [1].

2) CIPW-norm

3) Assumed to contain hydrous phyllosilicates resulting in a total water content of 3 wt. %.

4) Iron fraction to be varied from 34.4 (homogeneous model) to 95% (heterogeneous model).

Table 2. Shock recovery experiments, brucite[1)]

Sample No.	Sample Mass mg	Projectile velocity km/s	Impactor material	Peak pressure in stainless steel container GPa	Shock-induced water loss, wt %
16	21.4	1.70	Aluminum	23	≥59
18	21.7	1.08	Aluminum	13	18

1) initial water content: 25.4 wt % (theoretical: 30.9 wt %)

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Table 3. Parameters for model calculations of iron-water interactions during accretion of the Earth

Model Number	Water content of silicate planetesimals wt %	Initial fraction of iron planetesimals %	Time for termination of iron accretion 10^8 yrs	Final FeO budget 10^{26} g	Final H_2O budget 10^{25} g	Remarks
1	3	34.4	1.6	7.16	0	homogeneous model
2	3	36	1.1	6.46	1.26	nominal model
3	3	60	0.7	5.60	4.92	heterogeneous model
4	3	95	0.4	2.43	11.67	heterogeneous model
5	6	34.4	1.6	14.30	0	homogeneous model
6	6	60	0.6	9.50	13.34	heterogeneous model
7	6	95	0.4	5.00	23.36	heterogeneous model